

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
3 March 2005 (03.03.2005)

PCT

(10) International Publication Number  
**WO 2005/019500 A1**

(51) International Patent Classification<sup>7</sup>: **C23F 1/46**

(21) International Application Number:  
PCT/EP2004/009304

(22) International Filing Date: 19 August 2004 (19.08.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/645,278 21 August 2003 (21.08.2003) US

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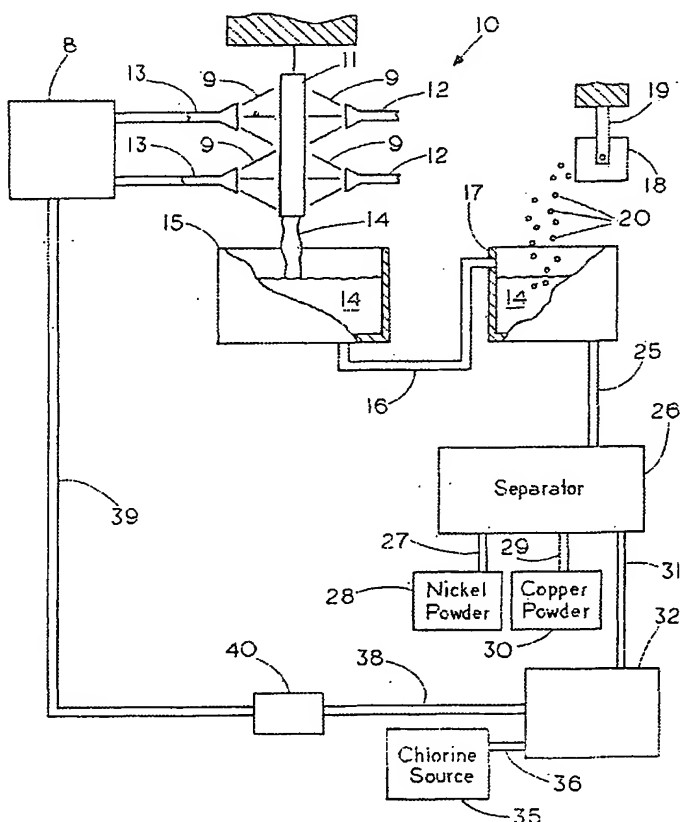
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(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
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TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,  
ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,  
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,  
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,  
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, ML, MR, NE, SN, TD, TG).

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(54) Title: METHOD OF RECOVERY OF METALS FROM ETCHING SOLUTIONS



(57) Abstract: A method of etching and a method  
of regenerating a spent etching solution compris-  
ing adding metal particles to a spent etching solu-  
tion to precipitate the residue metal or metals in  
the spent etching solution in the form of metal powders,  
removing the metal powders from the spent etch-  
ing solution and recovering the metals in the metal  
powders for future use. The remaining portion of  
the spent etching solution can then be regenerated  
to produce a fresh batch of etching solution.

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WO 2005/019500 A1



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**FIELD OF THE INVENTION**

This invention relates generally to etching and more specifically to the recover of metals from a spent etching solution.

**CROSS REFERENCE TO RELATED APPLICATIONS**

10 None

**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
DEVELOPMENT**

None

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**REFERENCE TO A MICROFICHE APPENDIX**

None

**BACKGROUND OF THE INVENTION**

20 The concept of etching or photochemical machining is well known in the art. Typically an etching solution is selectively applied to an article to remove unwanted material through a process of chemical interaction with the metal. One of the common etching solutions comprises a ferric chloride solution ( $\text{FeCl}_3$ ). The ferric chloride etching solution is used to etch a variety of materials including metals that contain iron, copper and nickel. The

25 etching is caused by the oxidative power of iron III ions. As a result of the etching process, the concentration of the nickel II and or the copper II ion increases in the etching solutions while the concentrations of the iron III decreases and the concentrations of the

iron II increases. Thus, as the etching process proceeds, the ferric chloride solution ( $\text{FeCl}_3$ ) reduces to a ferrous chloride ( $\text{FeCl}_2$ ) solution which contains metal ions through the interaction of the ferric chloride with the article being etched. The ferrous chloride solution can be converted back to a ferric chloride ( $\text{FeCl}_3$ ) solution through a process of regeneration which leaves a sludge of waste material. Although the ferrous chloride can be converted back into ferric chloride the etching process produces large amounts of waste or spent etching solutions which can contain large amounts of nickel and or copper. Generally, the sludge that remains from the regeneration must be carefully disposed of so as to avoid any adverse environmental impact. It would be preferable if the spent etching solutions could be refined to recover the metals in the spent etching solution. More specifically, If the spent etching solutions contains nickel and copper it would be preferable to recover the nickel and copper from the spent etching solution rather than having to dispose of the spent etching solution with nickel and copper.

The present invention comprises a process where the metals in the spent etching solution are separated and recovered from the spent etching solution by converting a residue metal, such as copper or nickel, to a metal powder. The metal powder can then be removed from the spent etching solution thereby decreasing the amount of sludge that needs to disposed of as well as allowing one to recover the metals for reuse.

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### SUMMARY OF THE INVENTION

A method of etching and a method of regenerating a spent etching solution comprising adding metal particles to a spent etching solution to precipitate the residue metal or metals in the spent etching solution in the form of metal powders, removing the metal powders from the spent etching solution and recovering the metals in the metal powder for future use. The remaining portion of the spent etching solution can then be regenerated to produce a fresh batch of etching solution.

### BRIEF DESCRIPTION OF THE DRAWINGS

The Figure is a schematic representation of an etching system having an etchant regeneration system that includes apparatus for separating etched metal from a spent etching solution and for regeneration of the spent etching solution to create a fresh batch of etching solution.

### DESCRIPTION OF THE PREFERRED EMBODIMENT

The Figure shows an etchant regeneration system 10 comprising a first etching stage wherein an article 11 is subjected to a spray of etching solution 9 from a set of spray nozzles 12 and 13. The fresh etching solution, which is contained in a container 8, is directed onto the article 11 through a set of spray nozzles 12 that direct etchant on one side of article 11 and a second set of spray nozzles 13 direct etchant on the other side of article 11. Although spray etching is shown, other etching techniques such as immersion of the article in the etching solution 9 can be used. The etching solution 9 removes unwanted material from the article, which is then carried away by the spent etching solution 14. The spent etching solution 14 and the unwanted material is then collected in a container 15.

In the etching of metals, a common etchant such as ferric chloride ( $\text{FeCl}_3$ ) is used as the etching solution. The removal of the metal from the article leaves a spent etching solution 14 comprising a ferrous chloride solution ( $\text{FeCl}_2$ ) containing a residue of metal and metal ions from the etched material. For example, if the article 11 contains copper the spent etching solution 14 contains copper and if the article 11 contains nickel the spent etching solution 14 contains nickel. The metals, which are normally included as part of the sludge, remain therein when the ferrous chloride solution is regenerated to produce a fresh batch of ferric chloride solution.

The regeneration of the ferrous chloride solution to produce a fresh batch of ferric chloride solution is known in the art. Etchant regeneration methods include the use of sodium chlorate and hydrochloric acid, ozone and hydrochloric acid, electrolysis with hydrochloric acid and use of chlorine gas. A method and system for regeneration of ferric chloride enchan

5 chloride enchan is shown and described more fully in U.S. patent 5,277,010.

In the present process the spent etchant solution 14, which contains metal and or metal ions is transferred, via a conduit to a second container 17. A pivotally mounted bucket carrier 18 which is suspend by a support 19 carries a number of metal particles 20 which

10 are shown be dumped into the spent etching solution 14 that is located in container 17. The metal particles comprise iron particles of various shapes and sizes. The particles can be in the form of sheets or wires. In general, it is preferred to have at least one dimension of the particle in the range of a millimeter to a centimeter. The process can be performed at room temperature or can be performed at higher or lower temperatures with the

15 temperature the primary factor in determining the rate of precipitation. The length of time to precipitate out the metal can range from a few minutes to hours depending on the amount of solution as well as the amount of residue metal in the spent etching solution.

In the present process iron particles 20 are submerged in the spent etching solution. As

20 the iron particles contact the etching solution the metal is precipitated from the spent etching solution in the form of metal powder. For example, with a spent etching solution that contains iron and residue metals such as nickel and copper it has been found that the addition of iron metal particles to the spent etching solution causes the nickel and copper in the etching solution to precipitate out of the spent etching solution in the form of metal

25 powders.

Once the spent etching solution 14 is subjected to the iron particles the spent etching solution 14 with the precipitate therein is directed to a separator 26 through a conduit 25. The metal powder can now be removed or separated from the solution with a separator through a process of sedimentation, centrifugation, filtration or similar process.

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In the preferred process the nickel powder is directed from separator 26 to a container 28 through a conduit 27 and the copper powder is directed from the separator 26 to a container 30 through a conduit 29. The copper powder and nickel powder can then be reused in the formation of copper and nickel metals. The spent etching solution, which now has the copper and nickel removed, flows into a container 32 through a conduit 31.

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The spent etching solution in container 32 can now be regenerated to form a fresh batch of etching solution. For example, with the spent etching solution comprising a ferrous chloride solution a source of chlorine 35 can direct chlorine into the ferrous chloride solution through a conduit 36 to convert the ferrous chloride solution to a ferric chloride etching solution. A conduit 38 and a pump 40 pump the batch of regenerated etching solution to the fresh etching solution 9 contained in container 8.

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Thus in the present invention the metal iron precipitates nickel and copper from used or spent etching solutions in the form of a metal powder that separates from the iron without forming adhering layers or large inter grown metal deposits. The process is based on the reducing power of metallic iron and it is believed the reactions for nickel and copper can be summarized as follows:  $\text{Ni}^{2+} + \text{Fe}_{\text{metal}} \Delta \text{Ni}_{\text{metal}} + \text{Fe}^{2+}$  and  $\text{Cu}^{2+} + \text{Fe}_{\text{metal}} \Delta \text{Cu}_{\text{metal}} + \text{Fe}^{2+}$  while the residual ferric chloride etching solutions is reduced according to the equation  $\text{Fe}^{3+} + \text{Fe}_{\text{metal}} \Delta 3\text{Fe}^{2+}$ . Thus the reduced solution contains  $\text{Fe}^{2+}$  ions and chloride ions. The solution can be oxidized by chlorine to produce a fresh Ferric chloride etching solution for further use.

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I claim:

1. A method of recovery of a metal from an etching solution comprising the steps of:
  - forming an etching solution containing ferric chloride;
  - 5 using the etching solution containing ferric chloride to etch a metal containing one or both of the metals selected from the group consisting of nickel and copper to form a spent etching solution containing metals of one or both of the metals selected from the group consisting of nickel and copper;
  - collecting the spent etching solution ; and
  - 10 placing iron particles in the spent etching solution to precipitate a metal powder of one or both of the metals selected from the group consisting of nickel and copper.
2. The method of claim 1 including the step of separating the metal powder from the spent etching solution through filtration.
- 15 3. The method of claim 1 including the step of separating the metal powder from the spent etching solution through sedimentation.
4. The method of claim 1 including the step of separating the metal powder from the spent etching solution through centrifugation. .
- 20 5. The method of claim 1 wherein the iron particles comprise particles having at least one dimension in excess of a millimeter.
- 25 6. The method of claim 1 including the step of maintaining the etching solution at a temperature less than the boiling point of the spent etching solution.



7. The method of claim 1 including the step of maintaining the etching solution at a temperature in excess of 0° centigrade.

8 The method of claim 1 including the step of removing the metal powder from the  
5 spent etching solution and adding chlorine to the spent etching solution to regenerate a fresh batch of ferric chloride.

9. The method of spent etching solution separation comprising:  
collecting a spent metal etching solution containing iron and a residue metal;  
10 introducing iron particles into the spent metal etching solution to thereby cause at least a portion of the residue metal to precipitate therefrom in the form of a metal powder;  
and removing the metal powder from the spent metal etching solution.

10. In combination;  
15 a container;  
a spent ferric chloride etching solution containing a residue metal therein; and  
a plurality of iron particles submerged in the spent ferric chloride etching solution,  
said iron particles submerged in the spent ferric chloride sufficiently long to precipitate  
the residue metal from the spent ferric chloride etching solution.

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11. The combination of claim 10 wherein the residue metal comprises copper to thereby precipitate copper metal therefrom.

12. The combination of claim 10 wherein the residue metal comprises nickel to  
25 thereby precipitate nickel metal therefrom.

13. The combination of claim 10 wherein the spent ferric chloride contains iron and a residue of copper and copper ions and a residue of nickel and nickel ions to thereby precipitate copper metal and nickel metal out of the spent ferric chloride solution.

5 14. The combination of claim 13 wherein the container receives the spent etching solution from an etching station.

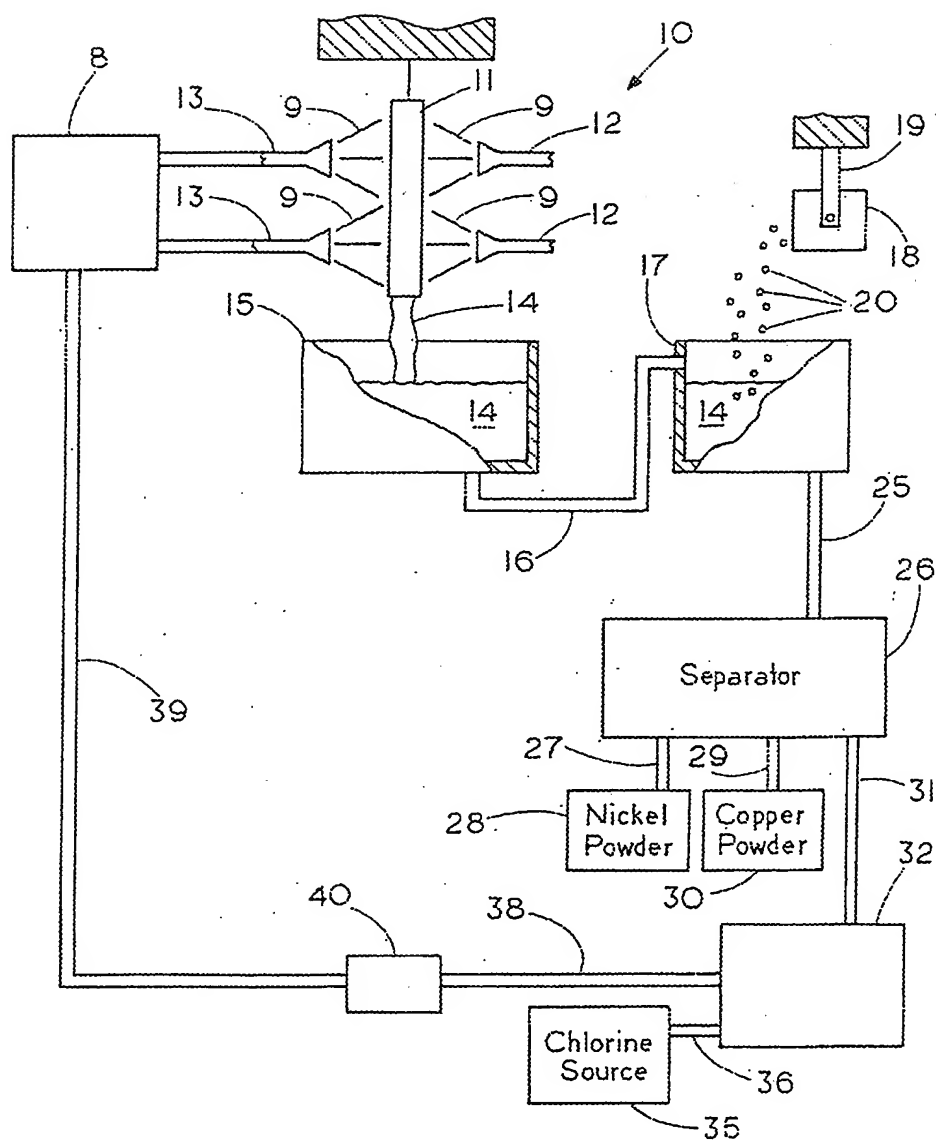
15. The combination of claim 14 wherein the combination is part of a system for etching, separation of residue metal and regeneration of spent etching solution.

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16. The combination of claim 15 wherein the spent etching solution contains iron.

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FIG. 1



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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/009304

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C23F1/46

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 431 (C-640), 26 September 1989 (1989-09-26) -& JP 01 167235 A (DAISO CO LTD; others: 01), 30 June 1989 (1989-06-30) see page 206, col. 5 to page 207, col. 9 of the original application abstract  ----- -/--	1,6-16

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

3 December 2004

Date of mailing of the international search report

13/12/2004

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International Application No

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